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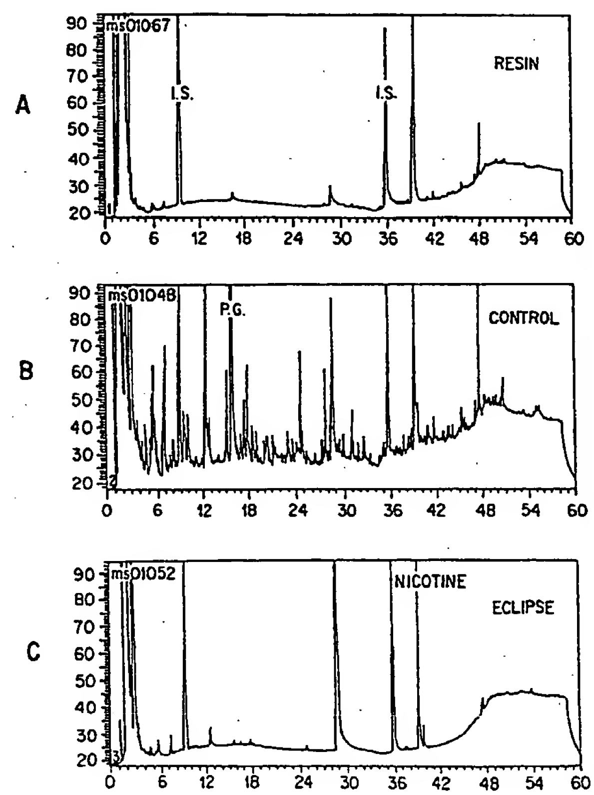
(54) Title: A METHOD AND APPARATUS FOR THE SELECTIVE REMOVAL OF SPECIFIC COMPONENTS FROM SMOKE CONDENSATES

(57) Abstract

Method and apparatus for providing an application of the principles of affinity chromatography in the design of cigarette filtration media to permit the planning and development of filter elements that selectively remove a class of target components of smoke. The filter elements are preferably silica with attached functional groups of the general formula: $R^1$–$(CH_2)_n$– where n is an integer from 1 to 40; and $R^1$ represents hydrogen, hydroxy, amine, amide, cyano, nitrate, nitro, thio, sulfide, sulfone, sulfoxide, I, Br, Cl, F or an alkyl or aryl organic substituent containing from about 1 to 40 carbon atoms, which may be straight or branched, saturated or unsaturated and optionally substituted with one or more substituents selected from O, N, S or halides.



# A METHOD AND APPARATUS FOR THE SELECTIVE REMOVAL OF SPECIFIC COMPONENTS FROM SMOKE CONDENSATES

## Field of the Invention

This invention relates, in general, to a chemical process and apparatus for the selective reduction of specific tar components of smoke generated by smoking articles such as cigarettes. More particularly, the present invention relates to the use of functionalized resin particles having a specific affinity for a targeted smoke component, such as tar, as a filter to selectively remove such component without coordinately removing desired nicotine and flavor components.

## Description of the Related Art

The control of tar and nicotine in cigarette smoke is largely attributed to the use of filters which physically remove total particulate matter (TPM) from the mainstream smoke condensate. Thus, the grades of "full flavor", "light", and "ultralight" cigarettes are based on the effectiveness of their filters to eliminate the potential tar and nicotine as found in normal unfiltered cigarettes. This classification system relates to the Federal Trade Commission's (FTC) restrictions on the amount of "tar" the cigarettes may deliver to a smoker. A "full flavor" cigarette delivers 14 mg or more of tar; a "light" cigarette delivers between 8 and 14 mg of tar; and an "ultralight" cigarette delivers less than 7 mg of tar. The "ultralight" cigarette also has an air dilution filter tip to further reduce the tar in the mainstream smoke.

The latest technology is a "heat" cigarette, available from R. J. Reynolds under the trade designation "Eclipse" which employs a carbon core in the cigarette. Unlike traditional cigarettes, this new cigarette does not burn at 800° C but instead heats the tobacco to less than 300° C. This low temperature avoids combustion which reduces tar formation and also the distillation of nicotine. The cigarette produces low levels of tar and nicotine in both the main and sidestream smoke. Toxicological and biological studies performed by Reynolds Tobacco Company have demonstrated that it is a safe smoking article. However, this cigarette does require some adjustment from the smoker.

In addition, numerous filter elements are disclosed in the art to be useful in reducing the levels of tar delivered to a smoker. For example, numerous patents exist describing filter elements that employ baffles and orifices to reduce tar and nicotine. U.S. Patent No 3,777,765 to Yoshinga discloses a filter apparatus consisting of a chamber for depositing smoke condensates. The smoke micelles route through this chamber and then exit through another porous barrier disk to become the mainstream

2,754,829 and 2,815,760 to Hess disclose the use of cationic exchangers, and US Pat. No. 3,093,144 to van Bururen discloses the use of both anionic and cationic resins to remove nicotine from tobacco smoke. U.S. Patent No. 4,700,723 to Yoshikawa and Shimamura also discloses a fibrous ion-exchange resin that can be incorporated into a cigarette filter. However, their approach is one dimensional. The gas chromatograms of the smoke condensate following the resin treatment appear to show only a quantitative reduction of tar and nicotine. There is no consideration of specificity and the disclosure does not address specific trapping of targeted components.

In U.S. Patent Nos. 2,920,629 and 2,920,630 to Kinnavy, a special cotton filter that is impregnated with a waxy salt of trimethyloctadecylammonium chloride ( or a class of long chain alkyl-quaternary ammonium chloride) and sodium sterate is disclosed as being useful as a cigarette filter. The input is roughly 1 gm per 2 gm of cotton. When this is used as a tobacco smoke filter, it drastically reduces both tar and nicotine. The high input of a waxy substance with cotton fiber apparently creates a sticky, fatty, and oily filter that obliterates the potential of the long chain hydrocarbon to be capable of specific interactions with smoke components. Instead, it is made into a sticky filter pad for the nonspecific removal of tar and nicotine. U.S. Patent No.. 3,033,212 to Touey and Kiefer discloses a similar intent of incorporating a waxy sterate into a cellulose filter to prevent smoke condensates from being dislodged from the cigarette filter after entrapment.

In the advent of ultra low tar cigarettes, there is a need to increase flavor and nicotine while decreasing tar. U.S. Patent No. 5,524,647 to Brackmann discloses using the upper portion of the tobacco plant to provide a higher than normal flavor to tar ratio. In addition, a cylinder of microfine filter element is used to reduce tar and nicotine. This biological approach tends to increase flavor and nicotine relative to tar levels.

U.S. Patent No. 5,465,739 to Perfetti et al describe the incorporation of acids and bases into the filter elements to influence the nicotine content of tobacco in the mainstream smoke. Acid is used for removing more nicotine in the tobacco blends which has high nicotine content and base for those tobacco blends with low nicotine. The intent is for normalizing the tobacco blends to achieve a consistent product.

Recently increasing pressure to reduce cigarette tar has reached an all time high. The industry has responded by increasing the efficiency of filters to decrease tar and nicotine. Nevertheless, many smokers demand for even further reductions in tar. However, the ability of existing cigarette design technology to respond to that demand, while still providing flavor, is limited. Conventional methods generally achieve a

composition of the mainstream smoke as it exits the cigarette. In particular, the invention provides an improved use of silica, in the form of functionalized silica resins having a high capacity bonded phase for the selective removal of specific classes of tar components to achieve a desired balance in a cigarette that is still full of aroma and flavor, yet offers slightly more nicotine than unwanted tar to satisfy a smoker. Additionally, the present invention alleviates concerns that smokers can defeat the beneficial attributes of reduced tar by the manner in which they smoke. Because the affinity binding of the targeted smoke component to the resin is practically irreversible, the present invention generates a mainstream smoke that is true to the intended label. The smoker can no longer change the manner of smoking to effect the composition of the mainstream smoke.

The present invention thus has multifaceted attributes, including the ability of resins with distinctive characteristics to be designed to bring about adsorption of only that population of tar components with such specificity. As a result, nicotine and tar can be regulated independently through the use of high capacity bonded phase silica resins. For example, a silica resin functionalized with a broad spectrum bonded phase, such as an eighteen carbon (C-18) aliphatic hydrocarbon, a catch-all resin, is uniquely suited for the removal of aliphatics and hydrocarbons from smoke, yet allows some polar flavor components to be delivered to the smoker. The C-18 bonded silica filter provides a reduction of the volatile and semivolatile smoke components equal to the standard of clean smoke generated by the no burn cigarette known as Eclipse, while maintaining an acceptable level of nicotine. The process is simple, safe, and efficacious. Since no chemical is added to the tobacco rod, no new chemical species are generated.

Additionally, the present invention provides cigarettes capable of delivering an artificial flavor, e.g., menthol, into the smoke by incorporating the flavoring into the resin particles such that they are removed in a "reverse mode" by smoke constituents exhibiting greater affinity for the functional groups on the resin particles. Consequently, the new generation of cigarettes with desired advantages can even deliver menthol flavor continuously with every puff and even to the last puff.

## BRIEF DESCRIPTION OF THE DRAWINGS AND TABLES

Figure 1 depicts chromatograms of the mainstream vapor-phase smoke of various cigarettes collected in a methanol trap: the top panel is smoke from a cigarette treated with a combination of resins consisting of : 50 mg silica (100μm and 60 Å), 100 mg C-18 resin (100μm and 60 Å), 100 mg of C-18 resin (200μm and 60 Å) and 100 mg

particle size and porosity is preferably selected so as not to increase pressure drop which increases draw resistance during smoking.

In general, specificity varies directly as the parameters of resin particle size, pore size, and resin capacity. The most selective resin therefore would generally have a large particle size (e.g., about 200 μm) a high porositity (e.g., about 1000 Å) and a high ligand loading capacity (e.g., at least about 1 milliequivalence per gram of resin). However, such a resin may be too fragile due to the thin walls created by the large pores in the particles. Accordingly, it is generally preferred that the selected resin be spherical or irregular particles having an average diameter of from about 35 to 400 microns, more preferably from 75 to 200 microns, and an average pore size ranging from about 60 to 1000 angstroms, more preferably from about 300 to 1000 angstroms. Additionally, the shape and size of the resin particles should be selected so as to enhance the interbead spacing to allow free flow of the smoke micelles.

To achieve a balance of efficiency and specificity, a preferred embodiment of the resin filter may employ a multicomponent resin cartridge. The first resin cartridge component preferably comprises a column from about 2-4 millimeters of a fine resin having an average particle diameter of from about 50 to 70 mm with a high porosity of from about 300 to 1000 Å to result in the gross reduction of tar and nicotine. The first component cartridge is preferably followed by a second component cartridge comprising a column of from about 5 to 10 millimeters in length of a relatively large bead resin have an average particle diameter of from about 150 to 200 μm, with large pore size of at least about 300 Å and a high capacity loading of functionality for specificity.

Alternatively, it is envisioned that a honey combed, filigree-like, or even fiberous construction of nonparticulate materials bearing functional groups may be used as a substitute. The ultimate criteria is to achieve high capacity of ligand bonding of at least about 0.6 millimoles per gram of material.

The ligand attached to the resin beads are preferably selected to preferentially bond with the molecules targeted for removal from the smoke stream. Although the specific functional groups utilized may vary widely depending upon the targeted smoke component, selection of suitable functional groups are well within the purview of one skilled in the art based upon fundamental chemical principles. However, with regard to the generally desired reductions of tar, preferred functional groups that exhibit greater affinity for tar than for nicotine have been found to contain hydrocarbon groups of the general formula $R^1$-$(CH_2)_n$-where n is an integer from 1 to 40; and $R^1$ represents

The following examples are illustrative of the present invention. The specific ingredients and processing parameters are presented as being typical, and various modifications can be derived in view of the disclosures as presented within the scope of the invention. Example 1 describes the basic strategies in the resin design. Examples 2-4, describes the solid phase affinity chemistry. The initial challenge to differentiate between nicotine and tar is borne out by the observation that nicotine is not retained by the reverse phase column. A specificity index is used to quantitate the differentiation and also to compare data between different groups of experiments. The resin experiments are recorded in the history of the mainstream smoke components in its passage through the compartments of resin, monoacetate filter and then collected onto a Cambridge filter pad. By studying the inter-relationship of the compartments, the molecular anatomy and the intricacies as well as the dynamics of the affinity smoke chemistry unfold. Additional confirmation of selectivity can be found in the Examples of amino and phenyl resins. The subtitles of selectivity are often difficult to recognize. This is due to the complexities in molecular recognition. Often it involves many functionalities and each contribute only a small percentage to the overall selectivity. The examples given are designed to provide the tools necessary to solve these intricate problems. Capacity and particle size parameters which enhance selectivity are discussed in Example 4. Example 5 validates the puff affinity technology by creating low or ultralow tar cigarette that burns rather than heats the tobacco and achieves a clean vapour phase composition which is comparable to the industry standard of Eclipse. Additionally, menthol cigarettes have been a commercial favorite, and Example 6 demonstrates the reverse mode of affinity resin utility for delivering this flavor.

**Example 1**

Silica is a very desirable solid phase sorbent and comes in various sizes and shapes. It can be either porous or nonporous, spherical or irregular, and with particle sizes that range from the very fine of 5 μm to the bead size of 1200 μm. Porous silica resin is the preferred material for the synthesis of a universal affinity precursor resin which possesses amino functionality. The arm of the precursor resin contains a 3 amino-propyl group which may be lengthened by reacting with various acyl-chlorides. For example, reaction with acetyl-chloride yields a resin containing a 5 carbon chain length functional group. In addition, more carbon chains may be extended to the amino arm by using fatty acids of different chain lengths.

The synthesis of the precursor resin began with selecting activated and porous silica resins with a mean diameter of either 50μm, 100μm or 200μm. The fines of the

pentadecanoyl chloride in pyridine. The next day, the resin was twice washed with methylene chloride and then three times more with methanol and dried.

**Example 2**

Chromatography of nicotine on C8 or C4 HPLC column under reverse phase condition showed that it was eluted in the void volume and was not retained by the column. This is due to the fact that nicotine is positively charged in an aqueous pH environment and does not bind to a resin which is specific for aliphatic carbon interaction. This fact makes it plausible to test if the nicotine present in the smoke condensate also behaves in the same manner. More specifically, the test may be conducted with C5 or C7 resins as manufactured under Example 1 in a "cigarette column." The resins used had an average particle size of 100 μm and a pore size of 60 angstroms. Table 1 shows the results of the experiments. The resins were placed between the filter and the tobacco rod of a conventional cigarette, and the cigarette was tested on a smoking machine. The control and resin treated cigarettes were smoked under standard FTC conditions. The puffing regimen consisted of 35 $\pm$ 0.5 ml puff volume, a puff duration of 2 seconds and a puff frequency of 1 puff per 60 seconds. In measuring the semivolatiles of the cold trap experiments, the cigarettes were smoked to 12mm from the overwrap. Smoke collection onto the Cambridge filter pad were extracted with 2-propanol. The determination of nicotine and propylene glycol was by capillary gas chromatography employing a HP5890 GC equipped with a 30 meter megabore carbowax column and flame ionization detector (FID). The semivolatiles were collected in a dry ice in isopropanol cold trap at -70°C and determined on a 30 meter DB624 capillary column equipped with a precolumn and also by FID detection. In the resin treated cigarette, the monoacetate filter was dislodged and removed from a commercial cigarette. The resins were weighed and placed right behind the tobacco rod from the open butt end of the cigarette. To insure even placement of the resin, the cigarette was kept in a vertical position, gently tapped, and a new and intact monoacetate filter reinserted. This experiment examined specific interactions between the smoke condensate and the resin. Therefore, the nonspecific trapping of smoke condensate was reduced in part by removing all the fines in the resins. The values of tar, nicotine, and propylene glycol, were all derived from the Cambridge filters.

Initially, the reduction of nicotine was compared to that of tar, however, any change in nicotine as a ratio to tar is insensitive because tar is at least ten times larger. In addition, tar is a poorly defined complex entity and its determination is not highly quantitative. The comparison should be to a specific indicator component of the tar such

**Example 3**

In the present example, the nonspecific entrapment of the smoke condensate was further reduced by using a more open resin with a bead size of 200 μm. In Table 2, the distributions of nicotine in the three compartments of the Cambridge filter, cigarette acetate filter and the recovered resin are shown.

**Table 2: DISTRIBUTION OF NICOTINE**

| *Resin Type* | Nicotine from Cambridge Filter Pad | Nicotine from Acetate Cigarette Fiber | Nicotine from Resin | Total Nicotine Recovered in mg |
|---|---|---|---|---|
| *Control* | 0.9167 | 0.6918 | n/a | 1.64 |
| *Silica -50 mg* | 0.8148 | 0.4386 | 0.1195 | 1.37 |
| *Silica -150 mg* | 0.7765 | 0.3383 | 0.2584 | 1.37 |
| *Amino - 50 mg* | 0.8913 | 0.4766 | 0.1059 | 1.47 |
| *Amino - 150 mg* | 0.8521 | 0.3768 | 0.3498 | 1.58 |
| *C 5 - 50 mg* | 0.9090 | 0.5246 | 0.1012 | 1.54 |
| *C 5 - 150 mg* | 0.8324 | 0.4316 | 0.3031 | 1.57 |
| *Phenyl - 50 mg* | 0.8888 | 0.4844 | 0.0658 | 1.44 |
| *Phenyl - 150 mg* | 0.9148 | 0.4541 | 0.2669 | 1.64 |

As shown in Table 2, due to the large bead size of the resins, nicotine on the Cambridge filters did not diminish greatly even when the resin input was150 mg. The total nicotine recovered in each experiment is the sum total of all three compartments. The upper limit (1.64 mg) is shown in the control experiment. In all the resin experiments, the total nicotine recovered approaches this value except for silica. This is

| *Resin Type* | % Control | | | % Reduction | | |
|---|---|---|---|---|---|---|
| | Nicotine | Propylene Glycol | Tar | Nicotine | Propylene Glycol | Tar |
| ***C 5 - 50 mg*** | 99.2 | 80.2 | 102.8 | 0.8 | 19.8 | -2.8 |
| ***C 5 - 150 mg*** | 90.8 | 51.9 | 92.3 | 9.2 | 48.1 | 7.7 |
| ***Phenyl - 50 mg*** | 96.9 | 64.2 | 92.3 | 3.1 | 35.8 | 7.7 |
| ***Phenyl - 150 mg*** | 99.8 | 54.3 | 92.3 | 0.2 | 45.7 | 7.7 |

Table 3 again demonstrates the differential removal of nicotine and propylene glycol in this very porous resin. The low percentage nicotine reduction makes it easy to contrast the over 50% reduction of propylene glycol. The carbon backbone of propylene glycol is C3, and this apparently accounts for its retention by the C5 resin. The phenyl ring as a rigid planar structure viewed from its side, is actually four carbons long. Together with the amino-propyl arm, the phenyl resin may actually behave like a C7 resin. This also accounts for its selectivity towards the propylene glycol. The 3-amino-propyl resin appears to have a two fold interaction with propylene glycol. The first is the propyl group of the resin with the propylene backbone. Then the resin amino group can hydrogen bond with the glycol-OH. Amino HPLC column is selective for carbohydrates and involves hydrogen bonding between N--H and the cis glycol O--H of carbohydrates. The duality of interactions suggests that the amino resin may show a slight advantage towards propylene glycol in comparison to the C5 and phenyl-resin. Table 4 summarizes the results of the specificity index comparisons.

Table 5: PHENYL - RESIN SELECTIVITY

| *Resin Type* | Benzene | Toluene | Phenol |
|---|---|---|---|
| | % Reduction | % Reduction | % Reduction |
| *Amino - 150 mg* | 43 % | 70 % | 78 % |
| *Amino - 150 mg* | 43 % | 52 % | 74 % |
| *Phenyl - 150 mg* | 68 % | 88 % | 64 % |
| *Phenyl - 150 mg* | 53 % | 79 % | 59 % |
| *C 5 - 150 mg* | 51 % | 76 % | 56 % |
| *Silica - 150mg* | 38 % | 56 % | 60 % |

All of the above data documents that "Affinity Smoke Chemistry" is valid and that the smoke components obey the principles governing the reverse phase column chromatography. This finding presents unique opportunities for the removal, or at least a reduction in, the level of all unwanted deleterious smoke components from the mainstream smoke of a cigarette.

**Example 4**

The main constraint of smoke chromatography is the flow rate of the puff passing through the resin column. Total flow under the FTC condition is 35 ml per 2 seconds; thus the flow rate is 1.05 liters per minute. The linear velocity of the flow over a 0.5 cm resin column is 2.1 liters/cm/min. This flow rate hitherto is very foreign to any conditions of chromatography, and the resin needs some special treatment to increase the probability of successful encounters between the smoke components and the functional groups. One parameter that directly relates to specificity is the density of functional groups on the resin. When smoke components are accelerating at such a high velocity, the abundance of functional groups may encourage more frequent collision, meandering, probing and testing to result in only high affinity binding. Density of functional group loading in the resin is noted as its capacity. Table 6 examines the resin capacity as a function of the specificity index for nicotine and propylene glycol.

This is consistent with the supposition that the higher the capacity, the easier it is to attain specificity.

The chromatography of smoke components on the resin is limited in time and space. Even at the optimum, the first and the last puff are less specific. When the smoke micelles of the first puff reach the resin surface, there is no competition and all components regardless of affinity can occupy a site on the resin. The last puff is equivalent to the final mobile phase load to the resin column with no additional washing. Each cigarette smoked according to the FTC method has a total of six to seven puffs. When the efficiency of the resin column is at its best, there is still roughly a minimum of 2 / 7 puffs or 30 % error. Experimentally, this was investigated by extracting the resin after a smoking session and studying the specificity of binding for the intended design of the column. Table 7 examines the bound nicotine and propylene glycol (p.g.) on the amino resins.

**Table 7: PARTICLE SIZE VS SELECTIVITY**

| Approx. Particle Size | | µg / mg resin | | Ratio |
|---|---|---|---|---|
| | | Nicotine | Propylene Glycol | Nic/PG |
| 60 µm | 30 mg | 14.52 | 12.52 | 1.16 |
| | 40 mg | 14.99 | 14.48 | 1.04 |
| | 50 mg | 12.99 | 10.18 | 1.27 |
| | 60 mg | 12.01 | 9.22 | 1.30 |
| | 80 mg | 9.31 | 6.53 | 1.43 |
| | 100 mg | 7.24 | 4.55 | 1.59 |
| 100 µm | 70 mg | 5.50 | 8.83 | 0.62 |
| | 100 mg | 4.89 | 7.15 | 0.68 |
| | 130 mg | 3.47 | 4.89 | 0.71 |
| 200 µm | 50 mg* | 2.12 | 6.24 | 0.34 |
| | 150 mg* | 2.33 | 4.81 | 0.48 |

* Assuming total recovery

As Table 7 illustrates, the resin design selects propylene glycol and excludes nicotine. The ratio of nicotine to propylene glycol equal to 0.34 is found in the last row of the table in the 50 mg resin experiment. This ratio indicates high selectivity for propylene glycol and it approaches the theoretical error limit as previously discussed. Ultimately, the superiority of the resin is only recognized for its outcome at the level of

chromatogram (bottom panel) in comparison to the unfiltered control cigarette is very simple. The most prominent species are: nicotine, glycerol, toluene, and benzene. However, many other smoke components between toluene and glycerol are clearly visible. Also observed are the volatiles that appear at the beginning of the chromatogram, before the benzene peak at 7.4 minutes. At the end of the chromatogram between 45-57 minutes a large number of low level components are indicated. The simple and clean vapor phase chromatogram of Eclipse is therefore a standard for purity of cigarette smoke.

In Figure 1, top panel, the vapor phase chromatogram of the C-18 puff affinity resin treated cigarette is shown. The resin composition consists of : 50 mg silica (100 μm and 60 Å), 100 mg C-18 resin (100 μm and 60 Å) 100 mg C-18 resin (200 μm and 60 Å) and 100 mg 3 aminopropyl resin (200μm and 60 Å), and thus contains silica, C-18 and amino functionalities. From visual examination of the chromatogram, it is readily apparent that the resin treated vapor phase is also relatively simple and clean. In particular, the multitude of semivolatiles and volatiles appearing between the I.S.(methyl-cyclohexane) and glycerol as seen in the control chromatogram are all absent, except for propylene glycol and a trace of toluene and phenol. The resins also have significantly decreased the highly retentive components which are eluted after 54 minutes. There are a few volatile species including benzene at the beginning of the chromatogram. At room temperature these components are very volatile and a small amount may even come off the resin during the smoking session and be retained in the cold trap. In contrast, there is a significant amount of nicotine still present in the smoke even after passage through such a broad spectrum specificity resin.

Figure 2 (middle panel) shows the vapor phase chromatogram of the combination resin consisting of: 50 mg 3 aminopropyl resin (100 μm and 60 Å) and 300 mg of C-18 resin (100 μm and 60 Å). The total areas of all the vapor phase components were summed and compared to the total integrated areas of the control (Figure 1, middle panel). The relative areas of the resin treated smoke components were 19.7 % of the control integrated areas. Therefore, the control methanol trap vapor phase content was diluted 1:4 and then subjected to GC analysis. The resultant chromatogram (Figure 2 top panel) is compared to the resin treated GC vapor phase chromatogram. The diluted control serves as a barometer in determining the efficiency of removal of any smoke component by the C-18 resin. The resin vapor phase profile should resemble the 1:4 diluted control chromatogram, if all smoke components is removed proportionately and non-specifically. Obviously, this is not the case, as the

Table 8: PRESSURE DROP MEASUREMENTS

| Resin or Filter | Pressure drop |
|---|---|
| Monoacetate Filter 20 mm | 2% |
| 300 mg 200 µm | 3% |
| Resin 50/300 (50 mg100µm 300 mg 200 µm) | 4% |
| Resin A (135 mg 100µm 200 mg 200 µm) | 5% |
| 150 mg 100 um | 6% |
| 200 mg 100 um | 7% |
| Resin S0 (150 mg 100µm 200 mg 200 µm) | 8% |
| Resin S08 (150 mg 100µm 200 mg 200 µm) | 8% |

The low tar delivery of the resin treated cigarette is not a result of non-specific physical trapping or to a high pressure drop. The 1:4 dilution of control smoke experiment clearly shows that it is due to differential binding. Further, the potential of this technology to produce different marketable cleaner cigarettes is illustrated in Figure 2. As Figure 2 (bottom panel) shows, a 150 mg of 100µm C-18 resin treated cigarette produces a vapor phase GC chromatogram comparable to that of the diluted control, differing primarily in that the nicotine content is almost doubled at 0.8 mg and the tar content is 14 mg. This is equivalent to a full flavored low tar cigarette, except that it has a much cleaner vapor phase smoke. For the 50/300 resin treated cigarette (middle panel), the nicotine content is 0.4 mg. It is equivalent to an ultra low tar cigarette with a higher than normal nicotine and flavor content. These experiments demonstrate the range of cigarette products that can be manufactured by simply adjusting the amount of C-18 resins in the filter.

**Example 6**

The displacement of nicotine by other strong binding smoke components in the puff affinity resin has been illustrated in many of the above experiments. These results suggest that extrinsic flavor can be delivered by a flavor cartridge to the smoker. The flavor can be delivered in large doses or made to release slowly. In the experiment, 50 mg of C-1 resin was loaded by melting 4.2 mg of menthol and 9.6 mg of vanillin in-situ. The resins were carefully placed behind the tobacco rod of a Marlboro cigarette as in the above experiments. The flavor cartridge immediately transformed the full flavored cigarette into a menthol cigarette. Figure 3 shows the mainstream smoke GC chromatogram of the smoke trapped on a Cambridge filter and extracted by 2-propanol.

WHAT IS CLAIMED IS:

1. An affinity chromatrographic filtration process for the preferential removal of one or more targeted components from cigarette smoke comprising:

a) selecting a ligand which exhibits a preferential affinity for said targeted components and which is capable of attachment to resin particles to form functionalized resin particles which preferentially bind said targeted components;

b) attaching said ligands to the surface of resin particles to form said functionalized resin particles; and

c) passing said smoke through a mass of said functionalized resin particles to preferentially remove said targeted components.

2. A process as recited in claim 1, wherein said preferential affinity of said ligands results from differences in charge between said ligands and said targeted components.

3. A process as recited in claim 1, wherein said ligands are selected from organic groups of the formula: $R^1(CH_2)_n$—

wherein: n is an integer from 1 to 40; and

$R^1$ is hydrogen, hydroxy, amine, amide, cyano, nitrile, nitro, thio, sulfide, sulfone, sulfoxide, I, Br, Cl, F, or an alkyl or aryl group of from 1 to 40 carbon atoms which is optionally substituted with one or more atoms selected from the group consisting of O, N, S, I, Br, Cl and F.

4. A process as recited in claim 3, wherein said resin particles proportionately reduce tar components of cigarette smoke more than nicotine.

5. A process as recited in claim 4, wherein n is an integer from 3 to 18 and $R^1$ is hydrogen.

6. A process as recited in claim 5, wherein n is 18.

7. A process as recited in claim 3, wherein $R^1$ is selected from the group consisting of benzyl, naphthyl and anthracene moieties.

8. A process as recited in claim 3, wherein $R^1$ is $NR^2_3{}^+$, with each $R^2$ individually selected from H, aryl, and alkyl groups of from 1 to 5 carbon atoms.

9. A smoking article capable of delivering a regulated smoke composition to a smoker, comprising:

a) a combustible filler wrapped in a combustible sheath; and

b) at least one affinity chromatographic filter unit designed to preferentially remove specific targeted components from said smoke disposed within said sheath adjacent to said combustible filler, said filler unit consisting essentially of a

21. A smoking article as recited in claim 20, wherein said nonfunctionalized resin particles comprise porous silica beads having an average diameter of from about 35 to about 75 microns.

22. A smoking article as recited in claim 9, further comprising a nonchromatographic filter unit consisting essentially of a mass of nonfunctionalized porous silica beads having an average diameter of from about 35 to about 75 microns disposed within said sheath and in flow communication with said affinity chromatographic filter unit.

23. A smoking article as recited in claim 22, wherein said affinity chromatographic filter unit contains a sufficient amount of said functionalized resin particles and said nonchromatographic filter unit contains a sufficient amount of said nonfunctionalized resin particles to reduce the tar content of the smoke delivered to the smoker to from about 0.75 mg to about 1.25 mg.

24. A smoking article as recited in claim 23, wherein the nicotine content of the smoke delivered to the smoker is from about 0.1 mg to about 0.3 mg.

25. An affinity chromatographic filter cartridge for selectively removing one or more targeted components from cigarette smoke comprising a hollow sleeve packed with resin particles bearing functional groups exhibiting greater affinity for said targeted components than for other components of said smoke.

26. A filter cartridge as recited in claim 25, wherein said resin particles are selected from the group consisting of silica, methacrylate, styrene and styrene divinylbenzene.

27. A filter cartridge as recited in claim 26, wherein said resin particles are porous silica beads.

28. A filter cartridge as recited in claim 27, wherein said resin particles have an average diameter of from about 35 to about 400 microns.

29. A filter cartridge as recited in claim 29, wherein said pores have an average diameter of from about 60 to about 1000 angstroms.

30. A filter cartridge as recited in claim 29, wherein said functional groups have the general formula:

$$R^1(CH_2)_n—$$

wherein: n is an integer from 1 to 40; and

$R^1$ is hydrogen, hydroxy, amine, amide, cyano, nitrile, nitro, thio, sulfide, sulfone, sulfoxide, I, Br, Cl, F, or an alkyl or aryl group of from 1 to 40

carbon atoms which is optionally substituted with one or more atoms selected from the group consisting of O, N, S, I, Br, Cl and F.

39. A process as recited in claim 38, wherein said functionalized resin particles proportionately reduce tar components of cigarette smoke more than nicotine.

40. A process as recited in claim 39, wherein n is an integer from 3 to 18 and $R^1$ is hydrogen.

41. A process as recited in claim 40, wherein n is 18.

42. A process as recited in claim 38, wherein $R^1$ is selected from the group consisting of benzyl, naphthyl and anthracene moieties.

43. A process as recited in claim 38, wherein $R^1$ is $NR^2_3{}^+$, with each $R^2$ individually selected from H, aryl, and alkyl groups of from 1 to 5 carbon atoms.

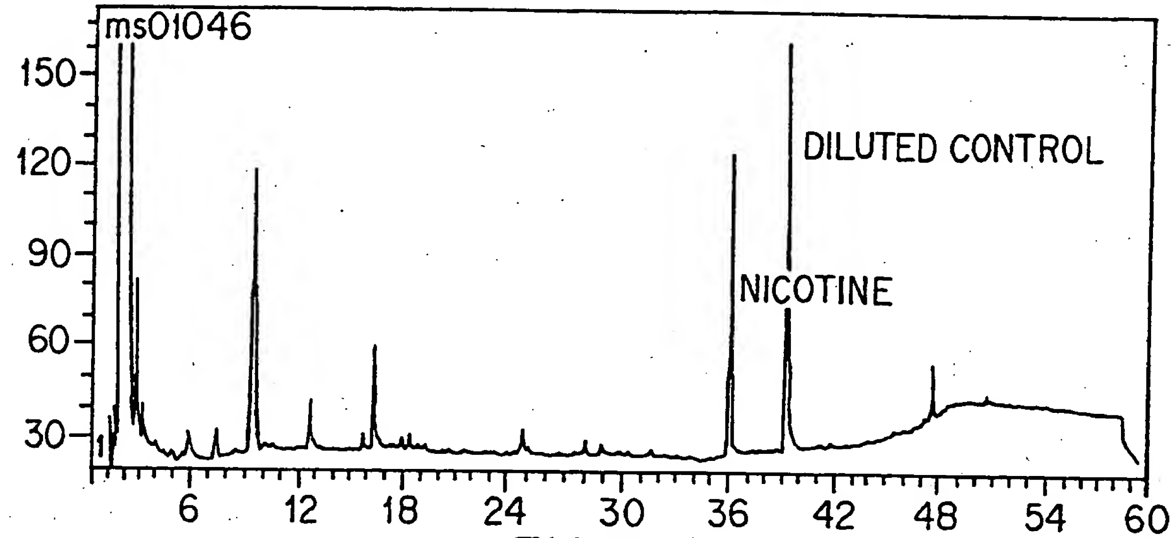



FIG. 2A

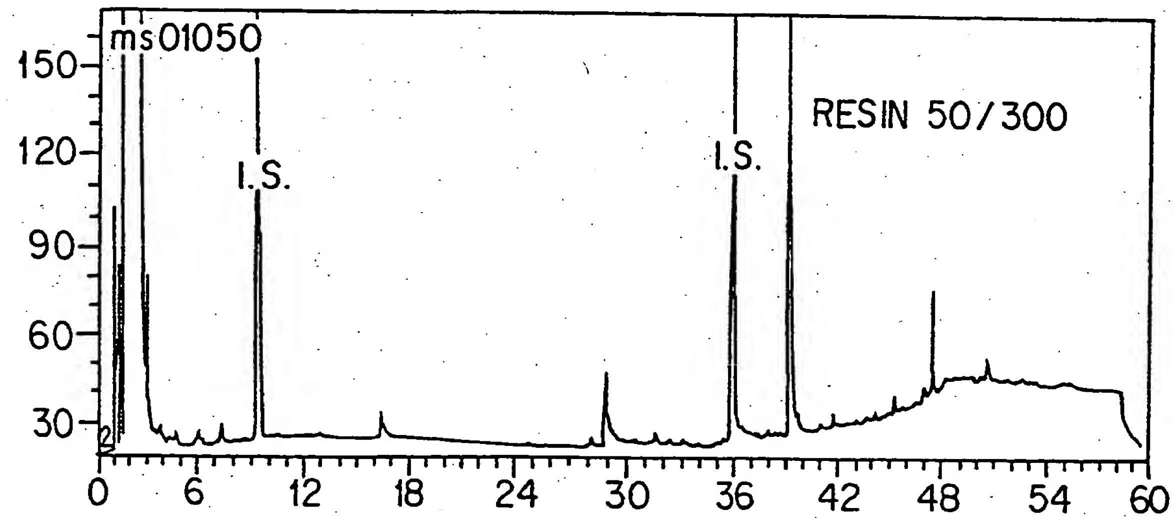



FIG. 2B

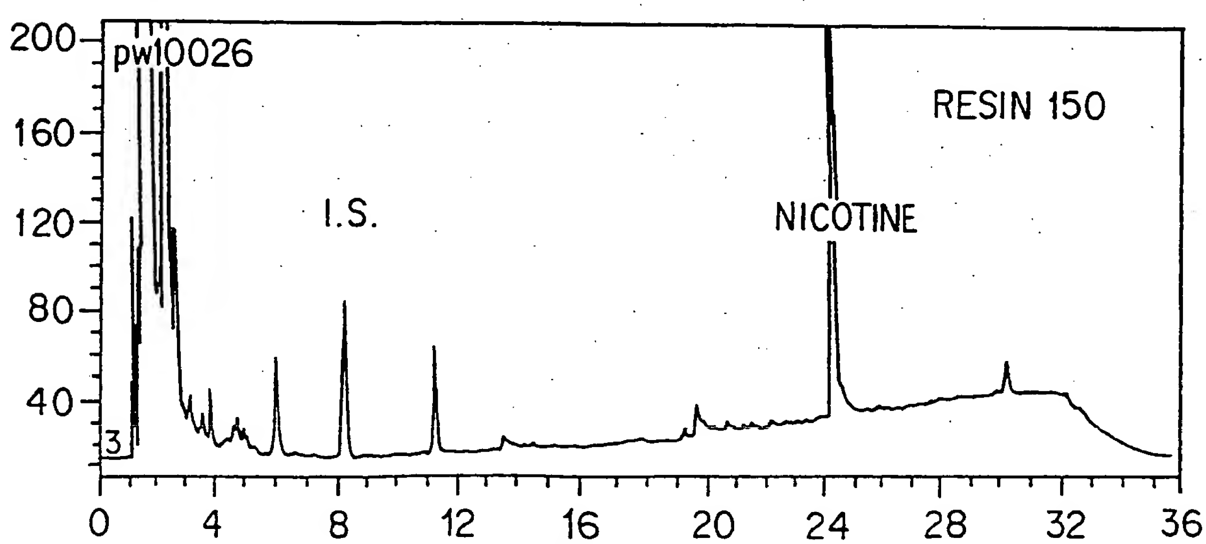



FIG. 2C

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/27188

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : A24B 15/18; A24D 3/04, 3/08, 3/12, 3/14
US CL : 131/334, 340, 331
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 131/334, 340, 331, 341, 200, 201, 202, 203, 342, 332

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | US 3,319,635 A (STAHLY et al) 16 May 1967, See Cols. 2-3. | 1-43 |
| Y | US 3,105,500 A (WILSON et al.) 01 October 1963, see entire document. | 2-8, 16-18, 22-24, 30-33, 37-43 |
| Y | US 4,033,361 A (HORSEWELL et al) 05 July 1977, see entire document. | 12-24, 28-33 |
| Y | US 4,201,234 A (NEUKOMM) 06 May 1980, see entire document. | 19-21 |
| Y | US 4,318,417 A (HIROSHI et al) 09 May 1982, see entire document. | 34-35 |

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 03 MARCH 1999 | 17 MAR 1999 |

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